KENNECOTT UTAH COPPER

Test Plan for the Evaluation and Optimization of Metals Removal from Kennecott Utah Copper Acidic Mine Waters via Alkali Precipitation and Physical Sequestration.

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Date: March 21, 2002
Version D

0024

Preface

The Record of Decision (ROD) issued in December 2000 regarding the KUC South Facilities Groundwater Plume documented the preferred remedial alternative as containment and extraction of the acid plume, followed by treatment in a membrane treatment system (nanofiltration and reverse osmosis). The Remedial Design process follows the ROD and will produce a detailed design for implementation of the preferred alternative. This work plan is a part of the Remedial Design Work Plan (sections 3.1.3 and 3.6; KUCC, August 2001) and is intended to address (a) optimization of the water-treatment technologies; (b) recently observed fluctuations in the neutralization potential of the tailings from the Copperton concentrator, and (c) post-mine closure plans to handle treatment residuals when the mine and mill are no longer operating.

This work plan addresses primarily the management of the acid-plume waters within the Zone A groundwater plume. Neutralization of acidic mine-related waters is accomplished by mixing with tailings from the Copperton concentrator, which have historically contained excess neutralization capacity[1]. However, over the past year the neutralization potential of the tailings has decreased as a function of the ore that is currently being mined. After mining there would be no tailings, so a different approach to management of these waters would be needed then, too. When the ore/tailings do not posses the required neutralization potential, the acidic mine waters must be neutralized by adding lime to the tailings system. Finally, it may be that additional chemical and physical treatment processes would improve the performance and cost-effectiveness of the current treatment procedures. The purpose of this work plan is to explain the methods and procedures that will be used to evaluate the treatment of acidic mine water when the tailings line does not possess the requisite amount of neutralization potential. The data obtained from this study will also be used to evaluate the neutralization of acidic mine waters for post closure when tailings are no longer being produced, as discussed in section 3.6 of the Final Remedial Design Work Plan.

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1   EXECUTIVE SUMMARY

Chemical treatment methods for the removal of heavy metals from acid mine drainage (AMD) and contaminated groundwater sources are frequently encountered in the mining industry. The addition of lime to these waters to precipitate metal hydroxides and complex calcium salts is a standard treatment method, resulting in a solid sludge that may be subsequently landfilled separately, or if possible, co-disposed with mill tailings in the tailings impoundment.

Kennecott Utah Copper (KUC) has two major water sources, which require treatment prior to disposal: a) meteoric leachwater collected from the waste rock dumps; b) acidic groundwater from the acid plume in the Kennecott South Zone. These waters are unique due to their high contents of dissolved aluminum, which, together with other metals and non-metals, can be removed via treatment with lime. Upon such treatment, large volumes of metal hydroxide/gypsum sludges are produced.

KUC has studied chemical treatment methods for many years. The focus of the present work plan is to use lime to neutralize the water and produce sludges of acceptable quality, which can be mixed with the tailings stream and co-disposed in the tailings impoundment.

The work plan proposes bench and pilot scale testing to develop expertise in treatment of acidic mine related waters, specifically with an eye toward development of processes tailored to KUC's unique water qualities. This expertise will be gained through testing of varying feed, mixing and solids settling designs.

2 GLOSSARY OF TERMS

AMW - Acid Mine Water. Water that contains elevated levels of dissolved solids due to contact with artificially exposed ore bodies or waste rock dumps. This term is used interchangeably with Acid Mine Drainage (AMD).

APC - Acid Plume Concentrate – effluent from the concentrate side of the nanofiltration membrane process being performed on water extracted from acid well LTG1146 or other wells located in the area of the acidic groundwater plume. This stream has similar water quality to ESCS waters.

APW - Acid Plume Water – water extracted from the acidic groundwater plume in the Kennecott South Zone A.

Accuracy - a measure of the closeness of an individual measurement or the average of a number of measurements to the true value and includes random error and systematic error.

Bias - the systematic or persistent distortion of a measurement process that causes errors in one direction.

Comparability - a qualitative term , which expresses confidence that two data sets can contribute to a common analysis and interpolation.

Completeness - a qualitative term that expresses confidence that all necessary data have been included.

Core Parameters - the minimum wastewater quality and O&M performance parameters required to be measured.

East Side Collection System (ESCS) - The East Side Collection System was constructed to collect all waters, which passed through the East Side waste rock dumps, whether artificial or meteoric in origin. With the termination of active leaching, this system collects strictly meteoric waters and delivers them to the p-plant, where they are stripped of their copper content. ESCS waters make up one of the two major process influent sources.

Effluent - the treated liquid stream produced by a wastewater treatment technology.

Industrial Wastewater - wastewater that contains primarily process wastewater.

Influent - wastewater introduced to the wastewater treatment technology under evaluation for treatment.

Lime – CaO or burnt lime. Milk-of-lime solutions are made by mixing powdered burnt lime with water to make a slurry of $Ca(OH)_2$ via $CaO + H_2O \rightarrow Ca(OH)_2$.

Major metals – For the purpose of this test plan, the major metals are aluminum and magnesium.

Minor metals – For the purpose of this test plan, minor metals are zinc, iron, manganese and copper. (See also - trace metals)

Membrane Filtration Plant (MFP) – The facility southwest of the Bingham reservoir which uses nanofiltration and reverse osmosis processes to segregate contaminated waters into two streams, one of lesser purity than the feed stream, and one of greater purity.

Normally Distributed Data - data that form a bell-shaped curve when plotted as a graph; the mean is at the center of the distribution on the graph and the curve is symmetrical about the mean; the mean equals the median; the data are clustered around the middle of the curve with very few values more than three standard deviations away from the mean on either side.

Percent Recycle (% recycle) – the volumetric flow of return thickened sludge into the reactor, as a percentage of the feed rate of influent.

Percent Solids Recycle (% solids recycle) – The mass transfer rate of solids reporting to the reactor via sludge recycle divided by the mass transfer rate of solids to the thickener.

Performance Data - removal efficiency and effluent concentration data for core and supplemental parameters.

Precision - a measure of the agreement between replicate measurements of the same property made under similar conditions.

Protocol - a written document that clearly states the objectives, goals, scope and procedures for a study.

Quality Assurance Project Plan - a written document that describes the implementation of quality assurance and quality control activities during the life cycle of the project.

Representativeness - a measure of the degree to which data accurately and precisely represent a characteristic of a population parameter at a sampling point or for a process condition or environmental condition.

Residuals - waste streams, excluding final effluent (e.g., sludge, filtrate, rinseate) that may be continuously or intermittently discharged from the wastewater treatment technology.

Settling Rate – The rate at which sediment will move downward in a quiescent solution. The settling rate will be measured by the rate at which the surface of the slurry bed in a

graduated cylinder moves downward during the unhindered settling phase of a settling test.

Soda Ash – Sodium Carbonate, Na_2CO_3

Standard Operating Procedure - a written document containing specific instructions and protocols to ensure that quality assurance requirements are maintained.

Start-Up - The period from the time the wastewater treatment technology is put on-line until stable operating conditions are achieved.

Stable Operation - the period during which the wastewater treatment technology performs in a consistent manner following a start-up period, within the range of Experimental Design-specified operating conditions.

Supplemental Parameters - wastewater quality and operating and maintenance (O&M) performance parameters, in addition to the core parameters, that are necessary to verify system performance.

Target Constituents - wastewater parameters that are specifically removed by the wastewater treatment technology.

Test Plan - a written document that describes the procedures for conducting a test or study according to the verification protocol requirements for the application of a wastewater treatment technology at a particular site. At a minimum, the Test Plan shall include detailed instructions for sample and data collection, sample handling and preservation, precision, accuracy, goals, and quality assurance and quality control requirements relevant to the particular site.

Trace Metals – For the purpose of this test plan, trace metals are lead, cadmium, and arsenic. Although arsenic (if present) is most likely in complex anionic form as an oxide, it is included in the group of trace metals for editorial convenience.

Upset Condition - a condition that causes the wastewater treatment technology performance to exceed the range achieved during operation under the stable conditions defined by the Experimental Design. Such conditions may include, but are not limited to, equipment installation or operator error, unforeseen change in the influent wastewater characteristics, acts of God, or other unusual conditions. Sub-standard performance does not necessarily indicate the occurrence of an upset.

Verification - To establish evidence on the performance of a wastewater treatment technology under specific conditions, following a predetermined study protocol(s) and Test Plan(s).

Verification Report - a written document, prepared by Engineering Services, containing raw and analyzed data, QA/QC data sheets, descriptions of collected data, procedures and methods used in the verification testing.

Zone 2 water – water drawn from Zone 2 of the Bingham Reservoir with the water quality currently observed. This water contains roughly half the dissolved solids of ESCS water but has approximately the same elemental ratios.

3   SITE DESCRIPTION AND BACKGROUND

3.1   Description of Water Sources

The treatment of acidic mine-related waters originating from KUC's waste rock dumps and the acid plume poses a long-term treatment challenge. Flows of 800 to 1500 gpm are expected well past the lifetime of mining operations in Bingham Canyon. The main flows of water (500 – 1000 gpm) due to meteoric infiltration, exit the dumps on the east side of the pit and are contained and intermingled in the East Side Collection System (ESCS). Additional wastewater requiring treatment will be pumped from the acid plume and is termed acid plume water (APW).

Total dissolved solids in the ESCS, APW and APC range from 3 to 12 weight % (30,000 to 120,000 mg/l). The dissolved components include alkali cations such as aluminum, calcium, magnesium; and heavy metals such as iron, copper, zinc, and manganese. Lead, cadmium, arsenic and nickel are also found at low or sub-ppm levels. The main anionic component is sulfate. Table 1, below, lists metals concentrations of these sources as of June 6, 2001.

Table 1 – 6/7/01 Metals Content of APW, APC, and ESCS Waters

In units of mg/liter						
Source	**Al**	**Ca**	**Mg**	**Fe**	**Cu**	**Mn**
6/7/01 Acid Plume Water	2354	479	3422	652	139	384
6/7/01 Plume Water Concentrate, 40% recovery*	3877	825	4739	1126	229	659
6/7/01 ESCS (PPlant Feed)	4943	563	9451	625	358	433

Source	**Zn**	**Pb**	**Cd**	**Ni**	**Cr**
6/7/01 Acid Plume Water	145	0.61	0.94	26	0.53
6/7/01 Plume Water Concentrate, 40% recovery	234	0.91	1.49	41	0.77
6/7/01 ESCS (PPlant Feed)	194	1.06	0.55	35	0.84

In units of lb/1000gal						
Source	**Al**	**Ca**	**Mg**	**Fe**	**Cu**	**Mn**
6/7/01 Acid Plume Water	19.6	4.0	28.5	5.4	1.2	3.2
6/7/01 Plume Water Concentrate, 40% recovery	32.3	6.9	39.5	9.4	1.9	5.5
6/7/01 ESCS (PPlant Feed)	41.2	4.7	78.8	5.2	3.0	3.6

Source	**Zn**	**Pb**	**Cd**	**Ni**	**Cr**
6/7/01 Acid Plume Water	1.2	0.0051	0.0078	0.22	0.0044
6/7/01 Plume Water Concentrate, 40% recovery	2.0	0.0076	0.0124	0.34	0.0064
6/7/01 ESCS (PPlant Feed)	1.6	0.0088	0.0046	0.29	0.0070

> * The nanofiltration of acid plume water was at the time of this analysis running at a 40% recovery of permeate. The recovery rate will increase in the future with a corresponding increase in the dissolved metals level in the concentrate. This concentration gain will be offset by a reduction in the concentrate flow.

Non-ESCS waters from various sources inside the mine such as pit water, North Ore Shoot, Dry Fork Tunnel, Lark Shaft, and several miscellaneous flows also are acidic and fall under the general descriptor of AMW. However, their acidity is much lower and mainly due to the presence of dissolved iron, rather than aluminum. Because of this, the total acidity in these other mine waters is an order of magnitude lower than in ESCS waters, APW, and APC. Finally, the TDS levels in ESCS waters, APW and APC are also

much greater than any other waters on the property, again primarily due to their high concentrations of aluminum and magnesium sulfates.

3.2   Characteristics of Alkali Precipitates – Treatment Options

The presence of large amounts of aluminum in these waters leads to significant volumes of basaluminite or complex aluminum-calcium salts upon alkali addition to pH 5. Treatment to pH 6 will co-precipitate most of the iron and copper with the aluminum hydroxysulfate product. Subsequent increase of the pH to 10 with lime precipitates mainly gypsum, with iron, copper, zinc, and some manganese reporting to the sludge. Increasing the pH to 11 precipitates magnesium and the remnants of manganese and gypsum.

The efficient treatment of these waters requires the neutralization of acidic components via one of several means: an alkali neutralizing agent, a non-hydroxide chemical precipitant/sequestrant, electrochemical removal, solvent extraction, or evaporation and re-crystallization. All of the techniques have technological challenges that make them unsuitable for the removal of at least one of the contaminant species mentioned in the previous paragraph. For example, the use of an electrochemical method addresses only the removal of transition metal species, as the reduction potentials of alkali species (Ca, Mg, Al) are far above the potential required to hydrolyze water. Non-alkali precipitation reagents such as barium chloride for sulfate removal, or 8-hydroxyquinoline for aluminum, are too expensive or too toxic for long term, high mass sludge systems. H_2S (i.e. S^{2-}) treatment for copper and zinc could be an option, but it does not address the need for removal of aluminum and iron from solution. The option of solar evaporation and landfilling precipitated salts removes the reagent cost component, but introduces several other problems, such as: (a) the dedicated land area required; (b) liner application and suitability issues related to reclaiming the material once it is placed and dried without damaging the liner; (c) environmental issues regarding dust control. Of all the treatment options bulk pH adjustment is a broad technique that provides for removal of aluminum, iron, zinc and copper at a relatively low pH (6-8) and manganese, magnesium, calcium and sulfate at a higher pH (10-11).

The primary metallic components of pH adjustment sludge are dependent on the neutralizing agent used and the final pH of the slurry. Basic neutralization reagents that are even remotely economically viable include quicklime (CaO), soda ash (Na_2CO_3), limestone ($CaCO_3$), and ammonia (NH_3). Other alkali reagents such as hydrated lime ($Ca(OH)_2$), and caustic soda (sodium hydroxide, NaOH) are also commonly used as treatment reagents for AMD, but are not economically viable for large flow systems such as KUC's.

KUC has an additional source of base neutralization agent: the tailings thickener underflow at the Copperton Concentrator. The alkalinity in these tails is made up of unreacted lime residual from the milling operation, plus the natural alkalinity of the mill tails. This alkalinity is believed to be mostly in the form of carbonate minerals, and can be up to 2% by weight (as $CaCO_3$ equivalent), depending on the ore type being processed. High variability in the gross alkalinity of concentrator mill tails as well as a general stoichiometric deficit for some ore types make reliance on the mill tails alone for treatment of the total AMW stream problematic.

Sludges generated by the addition of burnt lime (as a milk of lime slurry) to AMW to a pH of ≤ 8.0 are composed mainly of complex $CaAl(OH)_x(SO_4)_y(H_2O)_z$ salts, ferric oxyhydroxides, and semi-stable copper and zinc hydroxide/sulfate adsorbates. These sludges, in general, settle and filter relatively well. The chemical nature of these precipitates is not fully defined, however, a report from CANMET[2] on the sludge treatment of AMD included detailed XRD data that showed the presence of distinct phases of CaAl minerals. These complex mineral forms are believed to co-exist with amorphous aluminum hydroxy sulfate phases.

Precipitates generated by treatment of AMW with soda ash (Na_2CO_3)exhibit compositional properties , which justify the investigation of this reagent's feasibility for long-term treatment. The settling and filtering behavior observed to date is not as good as that of lime precipitates, but research performed so far has not explored all possibilities for process optimization. The sludge contains less sulfate and calcium than milk-of-lime generated sludges, as well as containing less total sludge mass per aluminum equivalent.

Limestone ($CaCO_3$) treatment of KUC's AMD was studied by Hazen Research in the mid 1970s. The efficiency of limestone is the lowest of all the reagent choices, requiring up to three times the amount of bulk material compared to lime or soda ash to achieve the same treatment level.

Sludges generated from AMD sparged with gaseous ammonia are very fine and difficult to filter. The use of ammonia as a precipitant has been studied quite extensively by KUC Engineering Services. Use of ammonia "trades" ammonium ion for aluminum in solution, and results in a very high ammonium sulfate level in the supernatant from the precipitation process. The investigation of ammonia as a precipitation reagent will not be pursued in this work due to two major complications: a) ammonium ion may negatively impact the biological systems in the tailings impoundment at even low ppm levels; and b) an economical, comprehensive treatment for ammonia stripping from the treated water has not been developed.

3.3 Past/Current Testing of KUC AMD via Lime Softening

3.3.1 Historical Testing

Several studies have been completed that address the issue of pH treatment of KUC AMD. In 1974, Hazen Research studied the feasibility of mixing AMD with concentrator tails[3]. This study explored options including treatment with limestone or a dual-stage limestone/quicklime pre-treatment before mixing with concentrator tails. Treatment of post-tailings pond recycle to pH 9 was also investigated.

In 1995, Infilco Degremont (ID) performed a series of treatability studies on waters including Bingham Tunnel, Barrier Well (B1G951) and East Side Leachate[4]. At the time of the study, the B1G951 well had similar water quality to the current (October 2001) acid well composition. The purpose of the ID report was to find experimental sedimentation rates for the lime treatment of these waters and determine reagent demand for each target treatment level. The report also contained some analytical data illustrating the reduction in dissolved metal species with increasing pH.

Montgomery Watson Engineers were retained in July 1996 to write a composite evaluation of the two earlier reports, with recommendations and approximate costs for the construction of a treatment facility[5]. They relied more heavily on the Infilco report

for the analytical data necessary to make construction estimates, as it was more comprehensive than the Hazen report. The essential reagent demand required for treatment of AMD from these three reports is summarized in the following discussion.

The highest dissolved components (i.e. >1000 mg/l) in KUC AMD are aluminum, magnesium, and sulfate. In the lime treatment of these waters, there are two major thresholds, which are significant in terms of reagent cost and solids handling. The first threshold is the precipitation of aluminum, which occurs at pH 4.5 – 5.0. Gypsum (i.e. calcium sulfate dihydrate) precipitates to some extent throughout the whole pH range, but mostly from pH 8.5-11. Magnesium hydroxide precipitates at a pH of ~10 - 11. The minor elements of copper, zinc, and iron will be mostly removed with the aluminum. Cadmium and manganese essentially will be completely removed with the calcium and magnesium. Thus, two fundamental process options exist: 1) treat AMD to pH 8 and precipitate aluminum, copper, iron, most of the zinc and some of the manganese; or 2) treat to pH 11 and precipitate those metals plus magnesium, manganese, and sulfate.

According to the ID report, the lime demand for treating Eastside Leachate to pH 6 is reported to be 21,100 mg/l, or 176 lbs/1000 gal. Treatment of B1G951 well water to pH 6 requires 12,100 mg/l, or 101 lbs/1000 gal. Treatment of these waters to pH 11 requires 475 lbs/1000 gal for leachwater and 249 lbs/1000 gal for B1G951.

3.3.2. Current Testing.

KUC has already completed one round of lime treatment tests, which have yielded significant amounts of information regarding the lime treatment of APW. These tests were performed in a pilot scale lime treatment plant, which can treat between .2 to 2 gallons per minute of feed water. In these tests, APW was treated in single pass, sludge recycle, and stepped precipitation modes. The average lime demand for treatment in all of these configurations ran from 70-120 lbs/1000 gallons. Sludges produced in these tests were analyzed for metal leachability and passed TCLP testing.

3.4   Summary and Conclusions for Current Project Design

3.4.1   Lime Sludges

The process benefits of creating lime sludges at pH ~8 include:
* Rapid settling (2-5 gpm/ft^2)
* Rapid filtration thus reducing required filter press surface area, or allowing the use of less expensive filtration technologies than pneumatic dewatering presses.
* The presence of unreacted lime in the sludge may increase the long-term stability in case of tailings pond disposal.
* Removal of some sulfate as gypsum is achieved.
* Lowest reagent cost per reactive base equivalents.

The negative aspects of lime treatment include:
* Large sludge mass leading to high handling costs for a landfill disposal scenario.
* No known market value for the sludge, causing additional costs for on-site storage or landfilling, and no defraying of reagent cost.
* Requires the construction of a lime slaker, which increases reagent delivery costs.

4   PROJECT DESCRIPTION AND OBJECTIVES

4.1   Project Overview

The process of treating acidic mine-related waters with an alkali reagent is conceptually quite simple. The primary feed water is introduced into a reactor vessel, or the first of two reactor vessels in series. There it is mixed with milk of lime, maintaining a constant pH. The resulting slurry is then fed to the second reactor or a thickener, where the slurry is separated from the supernatant liquor by settling. Some of the sludge can be recycled to the primary reactor from the thickener underflow if desired. The remainder of the sludge is disposed of. The thickener overflow can be fed to a secondary clarifier to increase solids recovery and reduce suspended solids contents in the final effluent.

Currently, there are several ideas as to the ultimate fate of the sludge generated in this process. Each option imposes a unique set of constraints on the design of a large-scale treatment facility because of the different process configurations required to meet the treatment objectives. The purpose of the current test is to explore the different process variables within the basic process design, and record their effects on the nature (composition) and properties (settling rate, density, leachability) of the corresponding sludge products. This exploration will be performed by following a systematic routine containing the following steps:

1. Identification of relevant process variables.
2. Design of an appropriate test platform.
3. Continuous operation of the test platform and data collection.
4. Evaluation of data and further testing as indicated by obtained results.
5. Preparation of full-size plant cost estimates and designs, addressing each possible scenario for disposal/use of treated water and sludge.

Items 1 and 2 have already been completed. Items 3 and 4 have been completed for the evaluation of lime treatment of APW. Chapter 5 of this document contains a diagram and equipment description for the test platform currently running at KUC's pilot plant as of March 10, 2002. Chapter 6 describes in detail the relevant process variables and the analytical process used to determine their relative importance.

4.2   Test Objectives

The main objectives of this test plan are:
- Determine optimum sludge generation conditions for maximum settling velocity, filterability and stability toward leaching.
- Determine optimum design for maximum efficiency of lime usage.
- Generate reagent cost per feed unit, and estimate power and equipment needs for upscale to a large plant.
- Determine the impact of sludge precipitation and removal on the water quality of the total system (tailings impoundment, process water recirculation, discharge of excess water to the Great Salt Lake).

5   DESCRIPTION OF TEST SETUP

The test equipment will be set up in the northeast bay of the membrane filtration plant. The arrangement is schematically represented in **Figure 1** on the following page and consists of the components listed below:

5.1   Mixers, Tanks, and Pumps
Reagent preparation tanks, with mixers
Reagent feed pump
Wastewater feed pump
Reactor vessel, with reverse (upflow) mixer and draft tube
Flocculant addition pump (optional)
Polymer mix tank (optional)
Thickener feed pump
Thickener with rake and variable overflow draw-off points
Sludge recirculation pump
Sludge dewatering pump
Plate and frame filter press

5.2   Control Equipment
pH probe in reactor controls reagent feed pump
Level controller in reactor controls thickener feed pump
Level controller in thickener to control sludge withdrawal pump

5.3   Discussion of Logistics
The production of a filterable sludge centers on the methods of alkali reagent addition, recirculation of sludge from the thickener, and on reactor design. The volume of the test reactor can be changed by the use of draft tubes of varying heights. Favorable sludges can be removed from the thickener underflow, or at some higher level in the thickener cone closer to the top of the sludge bed.

The fate of the solids generated in the final process is still undecided, however, the three most likely scenarios are: 1) addition to the tailings line; 2) dewatering and placing into an appropriate repository; or 3) dewatering, drying, and sale. The thickener overflow may be sent to a separate clarifier for further solids removal, or else put directly into the tailings line. Each of these scenarios puts different requirements on the quality of the sludge and remaining liquid. Therefore, this testing will collect data in a broad enough range that planning for each of these scenarios can be performed.

Reagent will be mixed in dual stainless steel tanks (120 gallons), by high-speed mixers. The use of two alternating tanks will allow for uninterrupted test runs of indeterminate length. .

The reagent feed will be controlled via a feedback loop from the pH meter in each reaction tank to its corresponding reagent pump.
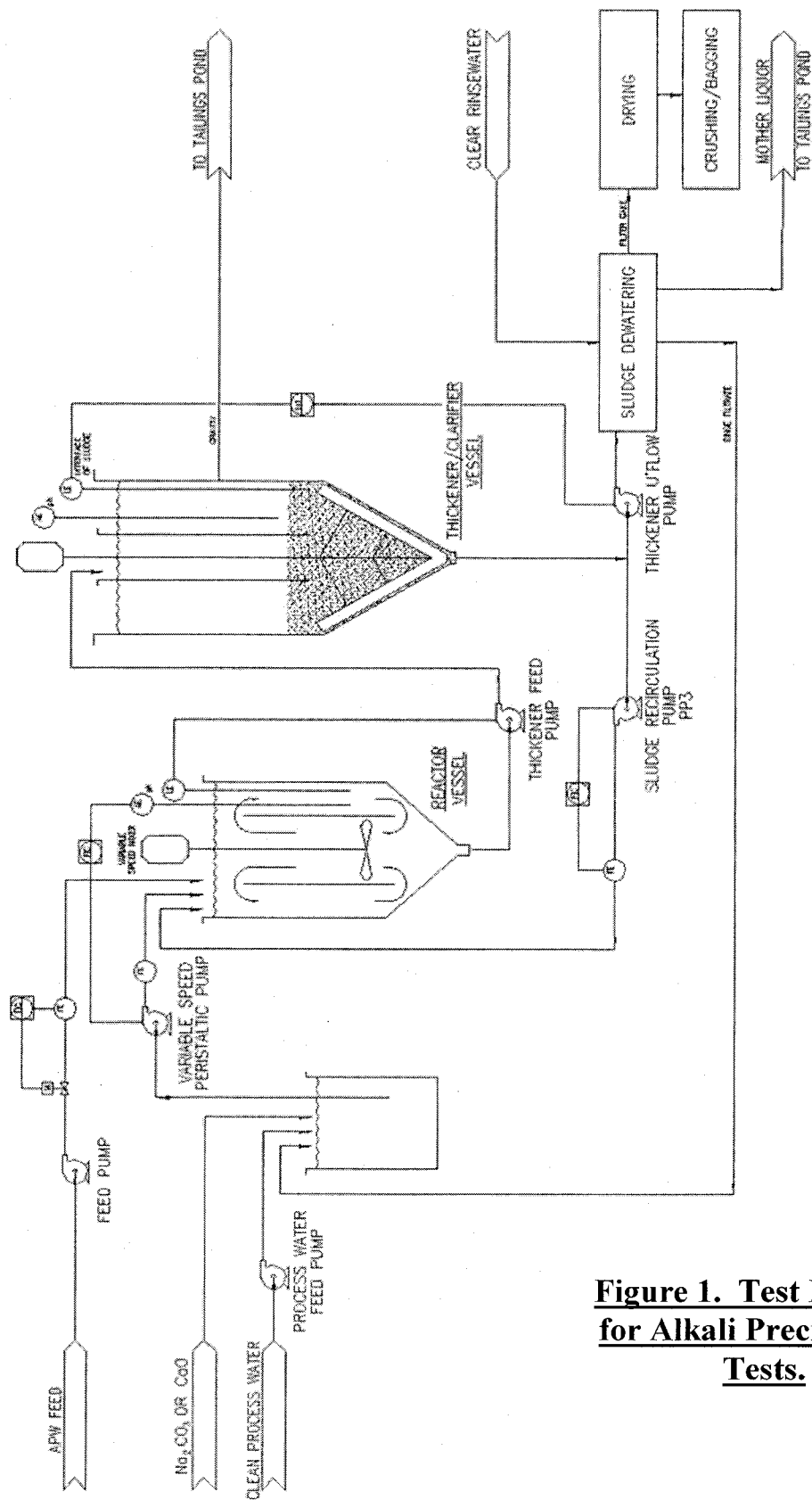
Figure 1. Test Platform for Alkali Precipitation Tests.

TO TAILINGS POND

CLEAR RINSEWATER

DRYING

CRUSHING/BAGGING

MOTHER LIQUOR
TO TAILINGS POND

SLUDGE DEWATERING

THICKENER/CLARIFIER VESSEL

OVERFLOW OF SLUDGE

THICKENER U/FLOW PUMP

THICKENER FEED PUMP

REACTOR VESSEL

SLUDGE RECIRCULATION PUMP PP3

VARIABLE SPEED MIXER

VARIABLE SPEED PERISTALTIC PUMP

FEED PUMP

PROCESS WATER FEED PUMP

APW FEED

Na₂CO₃ OR CaO

CLEAN PROCESS WATER

The slurry level in the reactor chamber will be maintained at a fixed level to keep a constant reactor retention time via either continuous control on the thickener feed pump speed , or a simple on/off loop triggered by a level meter in the reaction vessel.

The amount of reagent feed required for the process will depend on the wastewater feed rate. In general, a quantity of 100 to 300 pounds reagent per 1,000 gallons of feed water will be required. The thickener will be fed from the reactor effluent via an adjustable center well, such that the lower edge of the well can be placed above, at, or below the sludge level. The placement of the bottom edge of the center well can be manipulated to allow for the use of the sludge bed as a secondary filter. For the pilot system, a "sludge filter" approach might be favored over the traditional thickener configuration, where the influent material exits the center well above the thickened sludge bed. The slurry recycle will be taken off the thickener at one of several points. A diaphragm or hose pump will be used to recycle the slurry to avoid high shear on the sludge particles.

Various types of presses will be used to dewater underflow from the thickener to determine the optimum configuration.

6   SAMPLING AND ANALYSIS

6.1   Core Parameters

A matrix of test variables has been constructed and will be systematically explored. The test variables are explained below. Listed first are the four variables identified as having the largest effect on the final characteristics of the sludge. These are hereafter referred to as "major variables". The first test series will explore the effects of changing the major variables. The second test series will explore the effects of changing the other (minor) variables and will be defined by the results of the first test series

6.1.1   Major Variables

Reactor retention time plays a strong role in the formation of high-density sludge particles. It was noted in recent bench tests at KUC that increased reactor retention time resulted in faster settling times and greater inclusion of metals into the final sludge. These results were consistent with those found in the CANMET report[2]. Therefore, in terms of thickener design and control of end product quality this variable will be explored.

Reactor pH is the primary control for addition of alkali reagent. The pH of the reactor is dependent on two factors: 1) AMD:reagent feed ratio, and 2) reactor retention time. The reaction of AMD components with lime or soda ash is not instantaneous, and may take 3 to 4 hours to get to 90-95% of the ultimate pH value, and as long as 12 hours to stabilize completely. Lime is especially slow to stabilize.

The **entry points for feed, reagents, and recycled slurry** to the reactor vessel may be of great importance in the sludge formation process. Various configurations will be tested as separate variables: (1) The incoming milk-of-lime is first mixed with recycled sludge, and the mixture is then fed to the reactor, where it is combined with feed water. (2) The recycled sludge is mixed with the feed water, and then fed into the reactor to be mixed with the alkali reagent. (3) The recycled sludge is split between the feed water and the alkali reagent where they are mixed separately and then combined in the reactor.

6.1.2   Minor Variables

The **% sludge recycle** was noted as being of great importance. It exerts effects not only on the physical sludge properties, such as filterability and settleability, but also on the chemical composition of the sludge solids as a whole. In the CANMET[2] report, the Canadian researchers stated that a recycle rate between 10 and 15% was optimal. Experimentation with recycle rates of 0 to 50% will be explored in this test.

The **solids density** in the reactor vessel is another important parameter in producing optimal sludge. Solids densities of 0.5 to 10 grams per liter were cited in one report. The selection of the solids density influences the final water quality. Since KUC APW waters in a single-pass treatment contains from 15-50 g/l solids, and in some cases 30 g/l, they lie outside the conditions, which have been previously studied. The solids

density is controlled by the % solids recycle, and as such, will not be a controlled variable but rather will be monitored as an effect of changing the % sludge recycle.

Optimization of additional process water demand will be a parameter studied in this test. Delivery of reagent in liquid or slurry form requires a significant amount of extra water. Proper rinsing of the sludge cake also requires process water. Under ideal conditions, this process water would be of relatively high quality in order to allow for efficient CaO slurring, and to keep from contributing contaminants to the precipitate in the case of filter cake washing. Costs for clean water may be significant on both ends of the process. Good quality water will get increasingly expensive. The additional flow added in with the reagent also is destined to become clarifier overflow, increasing the total volume of wastewater reporting to the tailings impoundment. The armoring of quicklime particles with ferric hydroxide and gypsum is of particular concern if poor quality water is used in the preparation of milk-of-lime solutions. High sulfate content waters (>2000 ppm) may reduce the efficiency of lime slaking due to armoring by inactivating the lime particle surfaces, and thereby increase reagent costs.

Polymer addition to the thickener to improve settling is another parameter that needs to be examined. Type of polymer and addition concentration are two variables that will need examination. A panel of non-ionic and anionic polymers is currently being considered by KUC to start this investigation. A favorable aspect of polymer testing is that it can be easily performed on the bench prior to upscale in the pilot process. Therefore, testing of polymers will be pursued parallel to the pilot settling tests.

6.2   Process Variable Prioritization

In summary, the main process variables of interest in this study are:

- **Reactor retention time**
- **Reactor pH**
- **Entry point for feed, reagents, and recycled slurry**
- **Method of reagent delivery (solution or dry)**
- **Thickener polymer type and dose.**
- **% Sludge recycle**
- **Solids density**

Time and cost considerations require that a focused test strategy be developed, which identifies those process variables that exert the largest effect on the resulting sludge, and to evaluate those variables first. These foundational parameters can be tested in full to find optimal sludge generating characteristics. Once these characteristics have been confirmed, the major variables will remain fixed, and the minor variables will be used to fine-tune the process.

In preliminary testing, it was noted that the reactor retention time and reactor pH exerted large effects on the nature of the sludge. Increased reactor retention time accelerated the sludge settling rate and increased the removal efficiency of minor metals. The manner in which the reagents are added to the process was noted in the literature to cause large differences in system performance. Selecting four retention time intervals to test, four pH levels, and four configurations of material feed, a test matrix containing 4x4x4 = 64 discrete tests is generated. Applying this matrix to both milk-of-lime and

soda ash treatments, the number of tests is 128. The execution of these tests, at one test per day, will require approximately 1.5-1.8 man-years of labor.

6.3   Selection of Test Values for the Core Parameters in the Test Matrix

6.3.1   Reactor Retention Time

The span of the four values chosen for the test matrix should include the practical minimum and maximum values. The minimum reactor retention time is, essentially, zero. The option of building a mixing chamber of small size is appealing for cost reasons. Therefore, the first case for a reactor retention time will be zero, or a simple mixing chamber with only one or two minutes of retention time. The maximum retention time is limited by capital costs for the full-scale treatment plant. For this test program, 120 minutes will be considered as an upper boundary.

6.3.2   pH Levels

The minimum pH level for the test is set by the need to remove all of the aluminum from the water. This can be accomplished by treatment to pH 5, which will then be the lower boundary for pH variation studies.

The maximum pH level is set by the offsetting factors of reagent use versus the need to remove sulfate, manganese, and magnesium. To completely remove all metals to equilibrium concentrations using lime, a pH of 11 is required. Treatment to pH 10 with lime will remove most of the sulfate and manganese, but will leave the magnesium in solution. Treatment below pH 10 will remove iron, copper, and zinc, but will incompletely precipitate manganese and sulfate.

In terms of cost, the removal of all metals through magnesium is prohibitively expensive. The reagent cost alone for lime treatment to pH 11 could be as high as $18 per 1000 gallons. Additionally, the high pH solution would be discharged into the tailings impoundment. During the operation of the concentrator, the excess alkalinity in the sludge discharge would possibly be absorbed, or negated by the absorption of atmospheric carbon dioxide resulting in the lowering of the pH. After concentrator operations cease, the combined sludge/overflow may be discharged into the tailings impoundment without the benefit of a buffering carrier. Since there is an upper discharge limit on the tailings impoundment of pH 9, continuous dumping of pH 11 supernatant or mixed slurry from the lime treatment process would require acid addition to return the pH into the circumneutral range.

In light of these considerations, the maximum reactor pH will be 8. This will allow for the removal of aluminum, and give some extra data points to determine the effect of increased pH on physical characteristics of the sludge.

6.3.3   Feed Configuration

Alkali reagent can be either fed into the reactor directly, or mixed with recycled sludge from the thickener. The feed water can be fed directly into the reactor, or it too can be mixed with recycled sludge from the thickener before entering the reactor. There are four possible combinations of these conditions, all of which will be tested.

6.3.4 Recycle Ratio

The recycle ratio is the flow of solids delivered to the reactor from the thickener divided by the total influent rate. The CANMET report[2] showed an optimum particle size distribution at 10% recycle. Recycle rates of 5 to 30% will be tested.

7   START-UP PROCEDURES

The start up procedures required for running a test focus on
- Equipment cleanliness
- Test-specific equipment setup
- Preparation of reagents
- Preparation of sample logs and sampling devices
- Sampling Procedures

Equipment cleanliness

Equipment cleanliness is very important, because the data collected from these tests can be skewed by cross-test contamination. All tanks must be cleaned and rinsed of sludge and process water after each test. All hoses must be cleaned by running several hose volumes of plant water through them via their associated pumps.

Equipment readiness

The equipment should be checked for functionality before starting a test. This means all pumps should be checked and variable speed pumps should be re-calibrated. Hoses and quick-connect couplings should be inspected for cracks and leaks. Leaky O-rings on the press should be replaced. Each pump and mixer should be started to determine functionality and confirm the absence of leaks.

Before each test, the operator should look at the process variables to be used for that test from the Test Run Specification Sheet. The pump flow rates should be set before the test using the pump calibration procedure. After the pump calibrations have been performed, the hose connections should be checked to ensure that the process is set up correctly. The operator will mentally walk through the system to confirm that all connections have been made correctly and are secure.

The monitoring equipment consists mainly of tank level meters and a pH meter. The pH probe(s) must be calibrated and the slope recorded in the appropriate notebook. The pH probe should be stored in storage solution when not in use. Tank level meters should be checked for functionality before every test.

Preparation of reagents

The reagents in use for each test will be prepared according to the Test Run Specification sheet. The reagents required for this test program are:
- Burnt Lime: mesh size to be established and kept constant.
- Soda ash: technical grade soda ash will be used out of the bag for slurry preparation, and fed directly for the dry reagent addition studies.
- Flocculating agent: a water-soluble flocking agent will be employed to accelerate settling of the sludges. This floc will be prepared in a concentrated solution that will then be metered into the process with a metering pump. The concentration and dose of the polymer solution will depend on the results of the polymer sludge settling tests.

8   SAMPLING AND ANALYSIS

8.1   Sample parameters

During the test, several parameters will be monitored. The classes of parameters monitored are process parameters, sludge composition parameters, and physical characteristics of the sludge.

8.1.1   Process parameters
- All pump flow rates.
- Sludge bed depth in thickener.
- Reactor pH.
- Reaction vessel liquid level (i.e. average retention time).
- % sludge recycle.
- thickener overflow pH.
- reactor impeller speed.

8.1.2   Sludge Composition Parameters
- Metals content: Al, Ca, Mg, Mn, Fe, Cu, Zn, Cd, Pb, As.
- Sulfate content.
- Carbonate Content.
- Resistance to metal leaching.
- Alumina forms (only for final tests) via XRD.

8.1.3   Sludge Physical Parameters
- Thickener feed % solids.
- Thickener underflow % solids.
- Settling rate curves.
- Filtered solids % moisture.

8.1.4   Feed/Overflow/Filtrate Parameters
- Metals content: Al, Ca, Mg, Mn, Fe, Cu, Zn, Cd, Pb, As.
- Sulfate content.
- Carbonate content.

8.2   Sampling Procedures

8.2.1   Slurry samples
Slurry samples destined for metals analysis will be drawn in duplicate from the thickener feed inlet and the thickener underflow in plastic containers. The volume of the slurry samples will be sufficient for transport to the laboratory for % solids, metals, sulfate, and carbonate analysis as described in section 8.3. Two 240-ml sample bottles will be taken at first, and if more sample is required, then the sample volume will be

increased accordingly. Because the nature of the slurry changes with pH, no preservative will be added during sampling.

The sampling valve should be opened and let run for 10-15 seconds to get a representative stream. The bottle should then be filled halfway up, swirled and dumped two times before collecting the final sample.

8.2.2 Overflow/Feed/Filtrates

Twice per day, the thickener overflow and clarifier overflow will be sampled. Two aliquots of each of these samples will be taken. One will be preserved with 2 ml of 1:1 hydrochloric acid, and the other will be unpreserved. The unpreserved sample will be used for TSS and carbonate analysis, while the preserved samples will be used to analyze for metals and sulfate.

Each sample container will be rinsed out twice with the material to be sampled prior to taking the final sample. For the preserved samples, 4 mL of 1:1 HNO_3 will be added to a 250 ml volumetric flask. The flask will then be filled to the mark with the sample water, inverted 10 times, and transferred to a sample container. The appropriate dilution factor will then be noted on the sample bottle to account for the 4 ml of acid solution added.

8.2.3 Process Data

Process data will be used by the plant operators to maintain conditions indicated in the test plans. These data will be initially recorded in the plant logbook and later transferred to the project database.

8.3 Analytical Methods

Analysis of the parameters listed in section 8.1 will be performed according to the methods shown in Table 2. Where possible, methods from the Standard Methods for the Analysis of Water and Wastewater Manual or the SW-846 methodology will be used. Custom methods that are more suitable to the process environment may also be used. For example, the % moisture, carbonate, and slurry TSS will be performed using custom methods as compiled in Appendix A.

Table 2: Analytical Methods for Analysis of Process Samples	
Parameter	**Method**
pH	4500-H
Sulfate	375.2
% solids	Appendix A, method A-1
Total As	3500-As, 3113 B
RCRA Metals Leachability	1311 (TCLP), or 1312 (SPLP)
Temperature	2550-B
Iron	3005A, 3010A, 3050A, 7380
Manganese	3005A, 3010A, 3050A, 7460
Copper	3005A, 3010A, 3050A, 7210
Zinc	3005A, 3010A, 3050A, 7950
Aluminum	3005A, 3010A, 3050A, 7020
Magnesium	3005A, 3010A, 3050A, 7450
Calcium	3005A, 3010A, 3050A, 7140
Cadmium	3005A, 3010A, 3050A, 7130
Lead	3005A, 3010A, 3050A, 7420
Inorganic Carbon (Carbonate)	Appendix A, method A-2

9 QUALITY ASSURANCE PROJECT PLAN

The main elements of the quality assurance project plan are described below. These elements may be changed during the pilot stage at the discretion of the testing organization.

9.1 Metals Analysis

The analysis of metals will follow the 3000 series RCRA methods. The quality control elements of this method are the analysis of a method blank, certified blank spike sample, high concentration sample in a matching matrix, low concentration sample in a matching matrix, and continuing calibration checks analyzed every 10 samples. The recoveries of each target metal as noted in sections 8.1.2 and 8.1.4 will be charted electronically. Working control limits of +/- $2s_{n-1}$ and absolute control limits of +/- $3s_{n-1}$ will be used to judge the acceptability of the data. The chart standard deviation (s) will be calculated from the previous 30 analyses of the respective QC sample type.

In the event an element displays an absolute control limit which exceeds +/- 5% of the absolute value of the analyte in the sample, and this variability is determined to be instrumental in nature, and does not display significant bias, a determination of the analyte in actual samples will be made in triplicate, and the average value will be reported.

9.2 Sulfate Analysis

The analysis of sulfate via the gravimetric determination of barium sulfate is run with an associated method blank and blank spike laboratory control sample. The presence of less than 5 mg/L sulfate in the blank, and a 97-103% recovery on the laboratory control sample validate each sample run. In some cases, samples will be run in duplicate to determine matrix specific precision.

9.3 Carbonate

The analysis of carbonate via conversion to CO_2 and measurement with an IR cell is described in the KUC Engineering Services lab method manual, and is attached to this document in Appendix A. Carbonate samples are routinely run in duplicate, and a calibration check standard is run at the end to determine system drift. The QC elements in this method are a minimum regression co-efficient of 0.998 on the four-point calibration curve, the analysis of a method blank, duplicate analysis for each sample with associated RPD limits, and analysis of periodic calibration check samples.

9.4 Solids Settling Rates

Solids settling rate curves are determined in duplicate from samples collected consecutively. There are no QC criteria for acceptance or rejection of these data.

9.5 % Moisture

% solids analyses will be run in duplicate. The determination of moisture is made per the method found in Appendix A of this document.

10   DATA MANAGEMENT, ANALYSIS, AND PRESENTATION

10.1   Data Management

Many data types will be collected during the tests. These data will exist in several sources at their generation. For example, raw metals data will exist as forms generated by the atomic absorption spectrometer and respective computer spreadsheets. Sulfate data will exist in the form of spreadsheets. Settling rate data will exist in the pilot plant operator's bench notebook and spreadsheets. Carbonate analysis data will be contained in the analysts' notebook, and percent moistures will be transcribed directly into a project spreadsheet. Data from leaching tests or other analyses performed by the central laboratory will be incorporated into each project spreadsheet by hand. To make data access easier, all of the scattered data will be compiled into a single electronic test workbook in a timely manner. The test workbook will contain all data necessary to evaluate the test. A narrative sheet at the front of the workbook will contain a description of test variables, a discussion of upset conditions and errata, and a summary of the conclusions. A data worksheet will contain all of the raw data and associated measurements required for calculation.

After a test is completed, the contents of the workbook will be hardcopied and archived, and a backup electronic copy will be either burned on a CD or copied onto a magnetic disk. The hardcopy archive will also contain copies of notebook pages, log sheets or any other pertinent handwritten information. The archive envelopes will be labeled with the test number, date of archival, the envelope number, and the total number of envelopes used to archive that test. The envelopes will then be submitted to the document control officer for storage.

10.2   Data Analysis

Data will periodically be compiled and analyzed by KUC Engineering Services to determine the direction of the general course of testing. Chemists and project managers will collectively analyze the data in regular meetings. These meetings will be held not less than once per month. The correlation between core parameters and process variables will be explored.

10.3   Data Presentation

The results of these tests will be summarized for quarterly reviews. For this purpose, graphical representations of water and sludge quality parameters versus process variable changes will be generated.

Once this testing program has been completed, a variety of ultimate treatment options will be defined and the process conditions necessary to produce the most favorable product will be evaluated. These criteria will then be used to estimate costs for plant construction, operation, and disposal/sale of solid material. The ultimate report from this project will include several options for the construction of a full-scale lime or soda ash treatment plant.

11 References

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10) United States Environmental Protection Agency Office of Research and Development. EPA QA/G-9 Guidance for Data Quality Assessment: Practical Methods for Data Analysis. QA97 Version EPA/600/R-96/084, Washington, D.C. January 1998

11) APHA, AWWA, Water Environment Federation (Mary Ann Franson, ed.). Standard Methods for the Examination of Water and Wastewater, 19th Edition. American Public Health Association, Washington, D.C. 1995.

12   Appendix A – Custom Analytical Methods

Method A-1.   Percent Solids in Slurries and Vacuum-Filtered Lime Sludges

I. Scope: To determine the percentage of solid material in lime precipitate slurry and the vacuum-filtered sludge generated from it.

II. Technical Considerations: Sludges generated from lime treatment of waters high in aluminum contain high levels of adsorbed water, even at temperatures exceeding 100°C. The selection of 110°C as the drying temperature is due to the need for a consistent temperature to be used, and not for an intrinsic property of the sludge that is obtained at that temperature. % solids calculations based on sludges dried at temperatures other than 110°C may not be comparable to % solids calculations made here.

III. Apparatus/Supplies:
- 9 cm glass fiber filters, <5.0 um nominal pore size.
- 9 cm ceramic filter funnel
- vacuum pump
- vacuum flask
- 11 cm glass weighing dishes
- reagent grade water.
- 100 ml graduated cylinder
- bench scale with +/- .001g readability
- drying oven set to 110°C
- squirt bottle
- vacuum source

IV. Methodology:

The density of the slurries, the equivalent dry solids load, and the percent solids in vacuum filtered cake are determined via the following method:

1) Pre-weigh four glass evaporation dishes with a dry 9.0 cm glass fiber filter on each. Record these weights in the operators' logbook.
2) Clean the 100 ml graduated cylinder and dry or shake off thoroughly.
3) Tare the cylinder on the top loader balance. (i.e. the balance reads "0.000" with the cylinder on the pan.)
4) Take the cylinder off the balance, and carefully pour in 100 ml of material sampled from the sludge discharge hose. Don't spill any sludge onto the base of the cylinder or on the outside. If this happens, wipe off the cylinder as much as possible, or dump it out, clean the cylinder, and try again.
5) Place the full cylinder on the balance pan. Record the weight in the operators' notebook.
6) Place one of the pre-weighed glass fiber filters in the vacuum funnel and apply vacuum.
7) Wet the filter to seat it in the funnel with some DI water from the squirt bottle.
8) Pour the contents of the cylinder you weighed in step (5) into the funnel.
9) Fill up the cylinder with DI water to the 100 ml mark. Put your hand over the top of the cylinder and swish the contents around until any particles that are stuck on the sidewalls are brought into suspension.
10) Pour this solution into the filter funnel when the liquid just barely disappears from the filter cake surface, and then re-fill the cylinder with DI water to the 100 ml mark. Pour this final wash onto the cake when the surface begins to dry.
11) Allow the cake to dry until the water drops exiting the bottom of the funnel slow down to less than 1 every 3 seconds or so. Remove the cake from the funnel with a metal scoop and place back on the numbered glass dish on which it was pre-weighed.

12) Place the dish, filter, and filter cake on the balance and record the weight in the operator's notebook.
13) Place the dish in the oven to dry for 12 hours.
14) Remove the dish from the oven, allow to cool, and weigh. Record the weight in the operator's notebook.

Calculations:

Slurry Liquid Density: $\rho_{slurry} = \dfrac{M_{sl}}{V_{slurry}}$

Slurry Solids Load: $Q_{sol} = \dfrac{w_{dry} - w_{tare}}{V_{slurry}}$

*Filter Cake % Solids $= \left(\dfrac{w_{dry} - w_{tare}}{\left(w_{wet} - 0.700 \right) - w_{tare}} \right) 100$

Where:

ρ_{slurry} = liquid density of the slurry,   units: g mL^{-1}
M_{sl} = Weight of 100 mL of slurry,   units: g
Q_{sol} = Slurry Solids Load, weight of dry sludge per volume.   units: g mL^{-1}
w_{dry} = weight of dry cake + filter + dish.   units: g
w_{tare} = weight of unused filter + dish   units: g
w_{wet} = weight of wet cake + filter + dish   units: g
V_{slurry} = volume of slurry weighed in step 4, usually 100   units: g

* a correction of 0.7 grams is made in calculating the wet weight, to account for the water content of the wet filter itself.

Conversions: lb/kgal = g/mL x 8337
                GPM = mL/min x 2.642E-04

Method A-2 Carbonate Analysis on the Dohrmann DC-80

I. Scope: This method is designed for the determination of wt % carbonate in sludge samples generated via the lime softening of acid rock drainage. Any pulverized sample may be analyzed via this method as long as the material will fully react with the acid solution in less than 8 minutes, and does not release CO_2 at a rate, which will saturate the detector.

II. Method: A dried, pulverized, sample of sludge is placed in a 40 ml glass sample vial, and mixed with DI water to form a thin slurry. The sample vial is then sealed with a Teflon lined cap that is plumbed such that an inert gas purges the liquid, sweeps the vial, exits the top of the cap, and through the Horiba CO_2 detector. When the signal at the detector reaches baseline, an aliquot of 1:1 HCl is injected into the sample vial, dissolving the sample and converting carbonate ion to carbon dioxide gas. The gas is then swept to the detector and the total signal over an 8-minute period is integrated. Carbonate content is then quantitated from an external calibration curve.

III. Apparatus:
The Horiba PIR-2000 was the standard detector in the Dohrmann DC-80 TOC analyzer. Modification of the plumbing of the DC-80 for the execution of this method is shown in figure 1.

IV. Materials:
1) HCl, reagent grade, 1:1
2) 1 ml glass syringe with Teflon plunger
3) 5 ml glass syringe with Teflon plunger
4) 40 ml tall VOA vials, or equivalent
5) 1/8" dia plastic transfer line
6) Rotameter, +/- 1% accuracy
7) > 1 MΩ reagent water
8) Analytical balance, 0.0001 g readability
10) Inert gas, either O_2, Ar, or N_2 with regulator
11) Sodium Carbonate (Na_2CO_3), reagent grade, solid.

V. Procedure:
A. *Preparation of Standards*
1) Weigh 1.768 gram of Na_2CO_3 into a 1L volumetric flask and bring to the mark with boiled reagent water. If the reagent water is free of inorganic carbon, this solution now contains 1 mg/ml reagent water. Transfer to a storage bottle and keep tightly capped.
2) Retain 50-100 ml of reagent water for blank analysis.

B. *Calibration of Apparatus.*
1) Set up apparatus as shown in figure 1.
2) Set the range switch on the Horiba PIR-2000 to setting "3", 0-0.25% v/v.
3) Add 10 ml of DI water to the sample vial .
4) Screw the plumbed cap onto the sample vial. . The inlet gas line should be below the surface of the slurry. Slowly adjust the gas flow through the rotameter until a steady stream of bubbles is formed in the sample vial. Note the rotameter setting. **It is vital that all measurements be made with the same gas flow through the sample cell.**
5) Watch the analog display on the analyzer. Initially, the signal will rise as the air in the sample vial is purged out, and then the signal will drop to a steady baseline.
6) Once the baseline level is reached, pull a 2 ml aliquot of 1:1 HCl into the 5 ml syringe.
7) Push the start button on the DC-80 to start signal integration, and then inject the acid into the sample vial through the septum top cap. Inorganic carbon (carbonate) in solution will be purged out in the low pH environment and measured in the analyzer.

8) Observe the signal level on the analog scale on the analyzer. The signal should go up, then drop back down at a slower rate. The presence of hard to dissolve materials in the sample will cause the signal to plateau and drop very slowly.
9) Wait until the machine beeps three times to indicate the measurement is complete. The measurement will be considered complete by the instrument if either: a) the time elapsed is 8 minutes, or b) The signal level drops to where it was when the start button was pushed.
10) Record the integrated "total absorbance"
11) Run two more replicates and average the resulting total absorbances.
12) Repeat steps 3-10 with the following solutions:

Std #	mL DI water	mL 1.0 mg/ml standard
Blank	10	0
1	9	1
2	8	2
3	5	5
4	2	8
5	0	10

13) Plot the concentration of standard in mg vs "total absorbance" and fit a function to the resulting curve, such that $R^2 > 0.998$. If the calibration curve appears to have a linear portion and a curved portion at higher concentrations, then increase the cell flow rate and re-calibrate. A calibration curve with a distinct break in slope indicates detector saturation has occurred at some point, and will not be accurate at high concentrations.
14) Run samples according to the procedure described below.

C. Sample analysis:

1) Pulverize ~5 grams of scale sample in a mortar.
2) Weigh out a reasonable aliquot of sample into a 40 ml sample vial. A reasonable amount of sample can be estimated by dividing 5 mg by the estimated weight fraction of carbonate in the sample. (5 mg represents the middle of the calibration range)
3) Add 10 ml of reagent water.
4) Analyze samples as described in steps V.B.4-V.B.11.
5) Calculate the absolute weight of carbonate ($m_{carbonate}$) measured for each sample from the calibration curve constructed in section V.B.13.
6) Calculate the wt % carbonate in the sample via the following equation:

$$wt\%_{carbonate} = \left(\frac{m_{carbonate}}{m_{sample}} \right) x100$$

where m_{sample} is the mass of sample weighed into the sample vial in step C.2

7) Calculate the average and report.
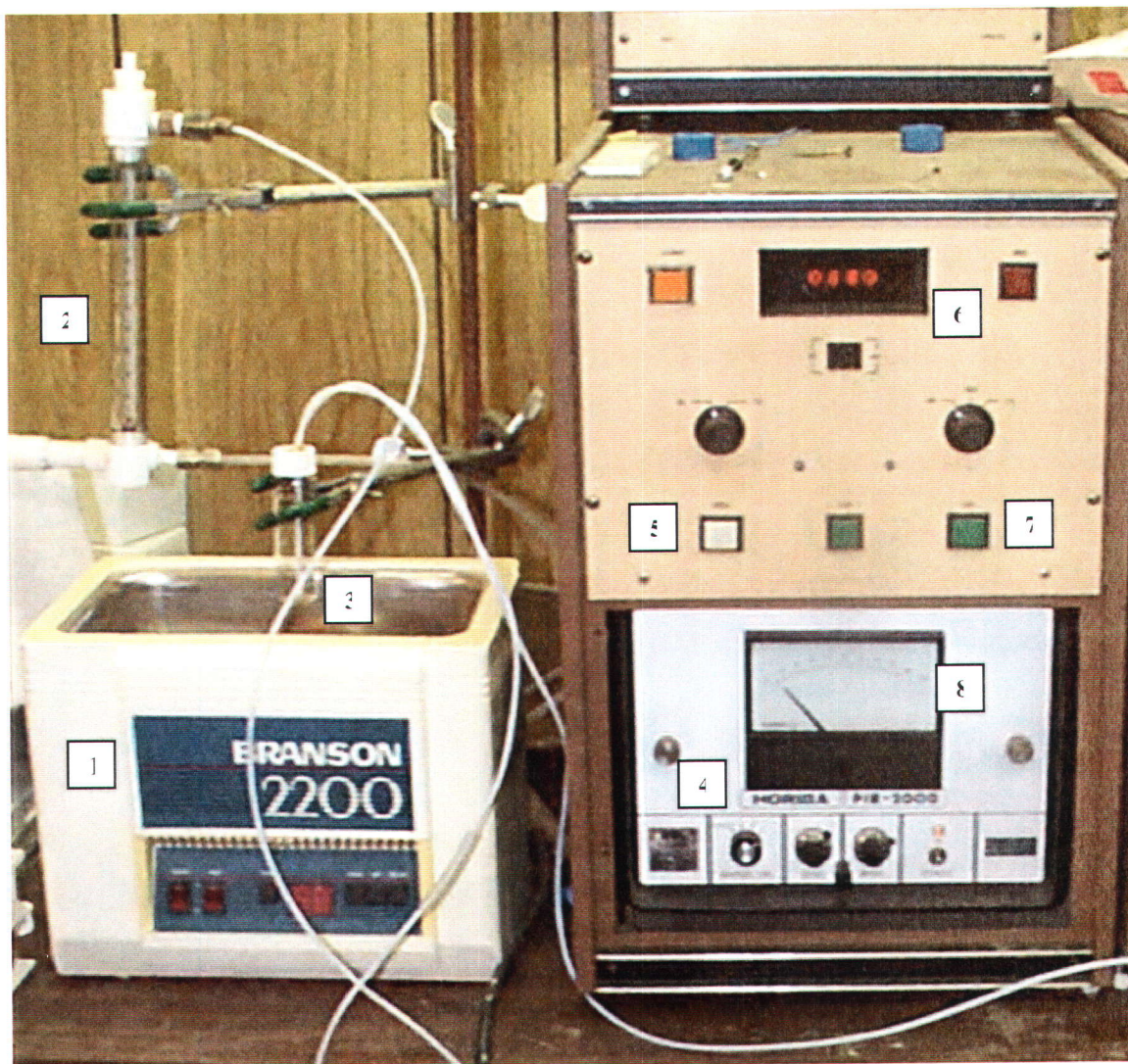
1. Sonicator
2. Purge gas rotameter
3. Sample purge vial
4. Detector range selector

5. Power switch
6. Integrator readout
7. Start switch
8. Analog detector signal display